

CHEMICAL REACTION STUDIES WITH A HYDROMAGNETIC SHOCK TUBE

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INTRODUCTION

To gain quick qualitative information about high-temperature reactions, the hydromagnetic shock tube originally designed by Fowler and later modified by Kolb has been found useful.⁽¹⁾ In this tube a shock wave is produced by the rapid discharge of a high-voltage condenser through an arc formed between two electrodes perpendicular to the tube axis and located at one end of the tube. Compared to the mechanical or diaphragm shock tube, the hydromagnetic tube is but a small toy, generally less than 2 feet long and having only one chamber. Series of equivalent shock waves can be passed through a gaseous reaction mixture and significant yields of product obtained. Effective contact times are very short (shorter than normally obtainable with an electric arc) and exceedingly high temperatures can be reached. These advantages are partly offset, however, by non-uniform shock velocity, the influence of the electric arc on the reaction, the requirement of low gas pressure, all of these making quantitative analysis of the entire process exceedingly difficult.

However, when the reaction products were stable and the reaction studied was one of high activation energy, much could be learned from a few experiments with the hydromagnetic shock tube. The only parameters determined were product composition and shock velocity. Details of the procedure, applied mostly to the pyrolysis of methane, are explained in the following sections.

APPARATUS

Figure 1 is a schematic drawing of our hydromagnetic shock tube. It is a modification of the so-called "Tee" or Kolb⁽²⁾ tube, the principal difference being that it is constructed of standard Pyrex pipe parts making for easy disassembling, cleaning, and exchanging. The electrodes along the bar of the tee-tube are connected in parallel with a high-voltage, low-inductance condenser (1.6 or 15 microfarads, 25 kv). A high-pressure gap, containing nitrogen between two stainless steel electrodes is interposed between one of the tube electrodes and the high-voltage side of the condenser to function as a switch. The entire tee-tube is filled with the gas mixture to be studied, which is usually at pressures of from 10 to 100 mm of Hg. To effect a discharge, the condenser is charged from a d.c. power supply and the gap switch triggered by means of an auxiliary electrode (not shown) brought to high potential by an automotive ignition coil attached to a battery. The discharge current returns to the ground side of the condenser through a strap located along the tee-tube between the two electrodes. As the current passes, it induces a magnetic field in the electrode section in a direction such as to produce an unbalanced force on the ions in the arc. This force propels the ions and the gas molecules colliding with them down the stem of the tee-tube. This "magnetic driving" accounts for about one-quarter to one-half the energy in the shock wave. Mainly, however, the shock wave is generated by the "pinch" effect of the discharge: The arc, constituting a rapidly varying current,

constricts about its axis ("pinch"), thereby heating the gas there to a very high temperature and bringing it to a pressure higher than that prevailing in the rest of the tube. Later expansion of this gas results in a shock wave propagating down the tube.

The dimensions of the apparatus were arrived at after considerable experimentation in which we tried to balance high shock velocity with convenience and safety of operation. The diameter of the tee-tube is 1 inch; the length of the stem portion can be varied by using different sections of pipe, but is usually between 1/2 and 2 feet; the gap between the electrodes is about 1/2 inch wide. All electrical leads are brass straps, 1-inch wide and 1/16-inch thick, to reduce inductance losses.

Shock arrival times were measured with a Tektronix Model 545A oscilloscope, using an inductive pickup (a few turns of wire) from the ground lead of the condenser to start the trace and a pressure or photo pickup at different locations along the tube to give an indication of the shock's position. Generally a Kistler piezoelectric pickup was used at the end of the tube where it faced the shock wave directly.

Figure 2 is a photograph of the apparatus during the passage of a very strong shock wave. The sharp, luminous front representing the farthest travel of excited ions and molecules is clearly shown. Figure 3 is the oscillogram for this particular experiment. The first sharp downward excursion of the trace corresponds to the arrival of the primary shock wave at the end of the tube, the second and third (smaller) excursions correspond to the arrival of the shock wave after traversal of 3 and 5 tube lengths, or — in other words — after 2 and 4 reflections at the tube ends.

THEORY

Fowler and coworkers^(2,3) were the first to investigate the phenomenon of the so-called "Rayleigh Afterglow," i.e., the luminosity produced outside of the electrode region in a short-lived gas discharge and lasting considerably beyond the duration of the discharge. They established that the afterglow was due to gas molecules excited by very intense shock waves originating in the discharge. Their shock velocity and luminous front velocity measurements were in general agreement with the theory of shock and detonation waves. Several years later, Kolb⁽⁷⁾ in an effort to produce very intense shock waves and thereby very high temperatures in deuterium (hoping to start a nuclear fusion reaction) modified the Fowler tube, chiefly by adding the return strap and other features to get the effect of "magnetic driving." Simultaneously, Harris⁽⁸⁾ developed a theoretical analysis of the Fowler tube by solving the following problem: "A given amount of energy W is deposited instantaneously in a very narrow slab of fluid in a tube of unit cross section. We wish to find the subsequent motion of the fluid." Using the methods of similarity analysis and approximations reasonable for strong shock waves (among others, that all the mass is concentrated at the shock front and that it has the velocity and internal energy prevailing there), Harris found that the shock radius R of a one-dimensional wave should vary with time according to the expression

$$R = \left(\frac{3}{2}\right)^{2/3} \left(\frac{\gamma+1}{2}\right)^{2/3} \left(\frac{W}{2\rho_0}\right)^{1/3} t^{2/3} \quad (1)$$

where γ is the heat capacity ratio (assumed independent of temperature) and ρ_0 the gas density ahead of the shock front. (Equation (1) is analogous to an expression derived by G. I. Taylor⁽⁹⁾ for the propagation of spherical blast waves in the wake of atomic bomb explosions.)⁽¹³⁾

Kash⁹ tried to check Harris' equation with the Kolb tube and found that an empirical relation between R and t , viz.,

$$t = AR^m \quad (2)$$

was a truer representation of his data than Equation (1), which, however, was in good agreement with the general trends (e.g., changes in W and Q). Recently, Agobian and Lifschitz¹⁰ have performed similar experiments and have come to agree with Kash. They also made a brief analysis of the reasons for the deviation of their results from Harris' formula.

Our own results with methane, nitrogen and other gases always showed agreement with Equation (2). However, under some conditions of low pressure and high discharge energy, our results have come very close to agree with Equation (1).

By combining the "blast wave" equation (Equation 1) with first order kinetics, it was possible to test at least the reasonableness of kinetic constants either assumed or found in the literature. While the procedure used was admittedly quite approximate, it proved to be consistent in itself and with other data in the case of methane pyrolysis. The theory behind it is, therefore, briefly sketched here and the method of calculation illustrated in Paragraph (f) of the next section of this paper.

Differentiation of Equation (2) with respect to time yields an equation for the shock velocity, viz.

$$\dot{R} = \left(\frac{1}{mA}\right)^{\frac{1}{m}} t^{\frac{1}{m}-1} \quad (3)$$

which is related to the ratio of temperatures behind and in front of the shock front by the "strong shock" formula¹¹

$$\frac{T}{T_0} = \frac{2\gamma(\gamma-1)\dot{R}^2}{(\gamma+1)^2 a_0^2} \quad (4)$$

a_0 and T_0 being the sound velocity and temperature in the medium ahead of the shock front. Equation (4) holds for $(\gamma-1)\dot{R}^2/2a_0^2 \gg 1$, a condition fairly well satisfied in our experiments over the region where reaction took place.

A monomolecular decomposition is described by

$$-d \ln c = k dt \quad (5)$$

where c is the concentration or partial pressure of the decomposing material, t the time, and k the reaction velocity constant defined by the Arrhenius formula

$$k = z e^{-E_a/R'T} \quad (6)$$

(z is the frequency factor, E_a the activation energy per mole, R' the universal gas constant, T the absolute temperature). By making the assumption of Harris and considering all the mass concentrated at the shock front, it is permissible to substitute T from Equation (4) into Equation (6) and use the resulting k in Equation (5). Thus one gets after integration:

$$\frac{1}{2} \ln(C_0/c) = \int_{t_0}^{t_1} e^{-BE_a t^{2-2/m}} dt \quad (7)$$

$$\text{with } B = \frac{(\gamma+1)^2 a_0^2 (mA)^{2/m}}{2R'\gamma(\gamma-1)T_0} \quad \text{and} \quad (7a)$$

$$A = \frac{4}{3} \cdot \frac{1}{\gamma+1} \cdot \left(\frac{2P_0}{W}\right)^{1/2} \quad \text{for } m = \frac{3}{2} \quad (7L)$$

The integral of Equation (7) can be written in the form

$$I = \int_{t_0}^{t_1} e^{-\alpha t^\beta} dt = \frac{1}{\alpha^{1/\beta}} \int_{\alpha t_0^\beta}^{\alpha t_1^\beta} e^{-y} y^{\frac{1}{\beta}-1} dy$$

$$= \frac{1}{\alpha^{1/\beta}} \left[\gamma\left(\frac{1}{\beta}, \alpha t_1^\beta\right) - \gamma\left(\frac{1}{\beta}, \alpha t_0^\beta\right) \right]; \quad \frac{1}{\beta} > 0;$$

where the incomplete gamma functions can be expressed in terms of confluent hypergeometric functions according to the formula

$$\gamma(C, x) = x^{C-2} e^{-x} (C-1) {}_1F_1[1; C-1; x] - (C-1) e^{-x} x^{C-2} - x^{C-1} e^{-x} \quad (9)$$

$$\text{When } n = \frac{3}{2}, \quad \frac{1}{\beta} = C = \frac{3}{2}$$

Equation (9) was derived from recurrence relations given in Slater's "Confluent Hypergeometric Functions." It is already in a form suitable for use with the tables contained in the same treatise.⁽⁴⁾

The isentropic index γ used in Equation (7) is an "effective" γ over the portion of the shock tube for which the reagent concentration is changed from C_0 to C by passage of the shock wave. Concentrations are found by analysis of the tube's contents, for varying tube lengths or varying positions of a barrier within the tube (cf., following section). Thus, extents of reaction in different portions of the tube can be calculated (shock strength attenuates with distance from the arc region).

EXPERIMENTAL RESULTS

(a) Relative Amounts of Reaction in Electrode and Shock Tube Portions

In order to determine the relative extent of reaction in the electrode and shock tube sections of the tee-tube, we placed a loosely fitting barrier in the shock tube at various distances from the electrodes in such a way as to reflect oncoming shock waves. The composition of the gas mixture after discharge was found to depend strongly on the position of the barrier. When the tube had been originally filled with methane, it was possible to double the proportion of acetylene in the final mixture by placing the barrier a certain distance from the arc (around 5 inches under our conditions). This effect of the barrier (the barrier did not change tube volume) was a maximum at a certain distance from the electrodes and decreased more sharply with decrease than with increase of distance from the position of maximum influence. The effect of the barrier dropped to zero at about five times the distance of the maximum from the electrodes. This effect on reaction rate we ascribed to reactions taking place in the wake of a shock wave derived from the primary shock wave by reflection at the barrier. When the barrier was far from the electrode region, the shock wave was too weak to cause further reaction; when it was very close to the electrode section, a shock wave had not yet formed and reaction was due to the arc.

By this procedure, we were able to estimate for the conditions of discharge voltage, pressure, electrode distance, etc., what the relative influences of arc and shock wave on the (high-temperature) reaction were and over what distance down the tube reaction took place.

(b) Effect of Increased Electric Energy Expenditure on Extent of Reaction

As mentioned earlier, the hydromagnetic shock tube permits passage of successive shocks through the same gas mixture. Thus it is possible to increase the energy input in two ways: (1) by increasing the discharge energy (higher capacitance, higher condenser voltage) and (2) by increasing the number of discharges per experiment, every discharge occurring at the same potential. Both methods increased the concentration of acetylene in the final gas mixture (analyses were done on aliquot samples from the tube either by mass spectrometry or by gas chromatography). However, the latter method was more instructive, for, as Table I shows, the gradual substitution of ethylene for acetylene was demonstrated. Table I also illustrates the effect of increase in shock strength by the introduction of "magnetic driving." When the return strap had been removed from the electrode portion, the yields of product were considerably lower.

(c) Effect of Initial Pressure on Extent of Reaction

As expected from the theoretical analysis (Equation (1)), higher initial pressures (higher p_0) should result in shorter shock radii at a given time (lower shock velocities) and hence lower temperatures and less reaction. This result is indeed obtained (Table II). However, probably because the methane decomposition reaction proceeds with an increase in volume, the decrease of acetylene concentration is even greater than one would otherwise predict.

(d) Shock Velocities

Figure 4 contains plots of arrival times in nitrogen of shock waves against breakdown voltage for various pressures. On the logarithmic scales, the curves are reasonably straight lines of slopes in agreement with predictions from Equation (1).

The variation of arrival time in methane with distance is shown in Figure 5. The curves are straight lines on a logarithmic plot. Thus the slope of these lines corresponds to n and the intercept to A of Equation (2). Over the distances shown, the exponent n is nearly independent of pressure and of breakdown voltage, as predicted theoretically. It is also nearly equal to 1.5, the theoretical value. A varies with pressure and discharge voltage according to Equation (1).

When a series of discharges and shock waves were passed through methane, arrival times at a fixed location changed as composition and pressure of the gas mixture changed, the result being a gradual decrease of arrival time or increase in shock velocity. By measuring both total pressure change and shock velocity for every shock passed through a given gas mixture, it was often possible to learn enough about the extent of reaction without further analysis; e.g., if one wanted to know what influence a change in the concentration of a particular reagent would have on the yield of a particular product.

An example of such a study is the effect of hydrogen on the pyrolysis of methane, which is illustrated in Table III. Increases in the hydrogen/methane ratio led to higher conversion of methane, but more to ethylene than to acetylene. The proportions of the products could be deduced from pressure and velocity measurements only.

(e) Pyrolysis of Hydrocarbons

The pyrolysis of methane in the hydromagnetic shock tube was used in the preceding sections to illustrate the method. Ethylene, acetylene, hydrogen and carbon were the principal products. Any change of conditions leading to an increase of temperature behind the shock wave (lowering of pressure, increase of breakdown

potential) resulted in an increase of acetylene and hydrogen production and a decrease of ethylene and carbon production. The converse was also found to be true. The heat capacity ratio of the higher paraffins is smaller than that of methane. According to Equation (1) the shock velocity should, therefore, be lower, which in turn would produce a lower temperature in the wake of the shock wave (Equation (4)). Thus, higher paraffins would be expected to yield relatively more ethylene and carbon than would methane under otherwise identical conditions. This was indeed the result obtained. Under the same conditions, however, olefins yielded more carbon than the corresponding paraffins. Evidently not only heat capacities but also energies of formation and kinetics of pyrolysis play an important role. When the differences of experimental conditions were taken into account, our work on hydrocarbon pyrolysis appeared to be in general agreement with that of Greene, Taylor, and Patterson, who used a conventional shock tube. Our pyrolysis work is still continuing and will form the subject of a later paper.

(f) Kinetic Parameters in the Pyrolysis of Methane

In a series of experiments with pure methane at a breakdown voltage of 16 kv and 60 mm of pressure, shock arrival times were measured as a function of distance along the tube axis and from the slopes and intercepts of the curves (Figure 5) the parameters $A = 0.512 \times 10^{-6}$ and $n = 1.5$ were obtained (cf., Equation (2)). For a distance of about 13 cm from the arc section (26 microseconds arrival time), an effective γ of 1.15 was calculated. (Because the value of n obtained was the theoretical one, it was possible to calculate the energies per unit area of shock front by differentiating Equation (1) and forming $Q_s R R^2$. For breakdown voltages of 10 to 18 kv, the ratio of this energy to the condenser energy proved to be very nearly constant (Table IV), thus lending further support to the validity of the blast wave treatment). Using literature values for the other quantities in Equation (7a), B turned out to be 0.322. Taking $E_a = 93$ kcal (a reasonable value), αt^B of Equation (8) came out 26.6. Taking a time spread of 10 microseconds, the integral of Equation (8) could be approximated by:

$$I \sim (t_i - t_o) e^{-\alpha t^B} \sim 10^{-5} \times e^{-26.6} \sim 10^{-16.6} \quad (10)$$

During this period about 1% of the methane was converted to other products (cf., Figure 6*); hence, from Equation (7)

$$z \approx \ln(C_o/C) \times 10^{16.6} = 10^{14.6} \quad (11)$$

This result for the frequency factor is in remarkably close agreement with Heath and Kevorkian's 1.32×10^{14} , considering the drastic approximations made. The error in z is probably about 2 orders of magnitude.

We do not recommend this procedure for the determination for reaction kinetics; many better methods are available.⁽⁶⁾ We have included this example only to illustrate the consistency of the description of the phenomena observed.

*The maximum in this figure is probably caused by shock wave reflections. Their effects have been removed in the above estimate.

CONCLUDING REMARKS

As said at the outset, the purpose of this paper was to illustrate a technique for the study of high temperature reactions. Accordingly, we have refrained from presenting many data obtained on specific reactions, especially since we have not yet arrived at definite conclusions. For example, our obtaining more carbon in the pyrolysis of methane than in the pyrolysis of paraffins of higher molecular weight under otherwise equal conditions could also be regarded as evidence in favor of Porter's theory of carbon formation.⁽²⁾ For, if acetylene is a necessary intermediate whose rapid polymerization leads to carbon, as Porter asserts, then molecules containing C_2 linkages would have a better chance of forming carbon. Much more evidence is needed to support or reject this speculation.

To obtain quantitative information, we recently inserted a diaphragm into the shock tube. It thus became a "conventional" tube, with the high-pressure section electrically heated by the arc discharge. However, it differs from the conventional shock tube by the higher Mach numbers and by the possibility of reflecting primary shock fronts arriving at the tube's end as rarefaction rather than compression waves (because of the great temperature difference in the two chambers at the time of diaphragm rupture). A method of "tailored interface" by adjusting tube length is thus made available. This work will be the subject of a later communication.

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TABLE I

Composition of Gas Mixture Resulting from Passage
of Series of Shock Waves through Methane

18 kv. Breakdown Potential
Starting Pressure: 60 mm Hg

	<u>Composition in Percent by Volume</u>				
	<u>Original</u>	<u>After 1 Shock</u>	<u>After 5 Shocks</u>	<u>After 20 Shocks</u>	
Magnetic Driving	---	Yes	Yes	Yes	No
<u>Constituents</u>					
H ₂	---	6.1	25.0	50.9	42.0
CH ₄	100	92.6	70.6	36.6	51.4
C ₂ H ₆	---	0.2	0.1	0.4	0.3
C ₂ H ₄	---	0.2	0.6	1.7	1.4
C ₂ H ₂	---	0.9	3.6	10.0	7.5
di-C ₂ H ₂	---	---	0.1	0.4	0.2
Final Pressure (mm Hg)	60	63	70	89	76
Arrival Time at Tube's End (μ secs.)	670	665	640	590	-

TABLE II

Effect of Initial Pressure on Product
Distribution of Pyrolyzed Methane

Composition after 20 Shocks of 18 kv. Breakdown Potential

<u>Constituents</u>	<u>Initial Pressure, Percent by Volume</u>		
	<u>20</u>	<u>60</u>	<u>120 mm Hg</u>
CH ₄	19.5	46.7	48.9
C ₂ H ₂	61.2	43.6	26.6
C ₂ H ₄	5.7	10.5	16.6

TABLE IIIEffect of Hydrogen on Pyrolysis of Methane at Constant Total Pressure

18 kv. Breakdown Potential

<u>Constituents</u>	<u>Composition after 5 Shocks in Percent of Methane Charged</u>		
	<u>No Initial H₂</u>	<u>10% H₂</u>	<u>30% H₂</u>
CH ₄	60.7	54.3	48.6
C ₂ H ₂	26.0	19.6	18.3
C ₂ H ₄	4.2	21.4	26.3
C	7.5	6.8	2.8

TABLE IVShock Arrival Times in Methane at 25 cm Distance as Functions of Breakdown Potentials

Breakdown Potential (kv)	6.0	10.0	13.0	16.0	18.0
Condenser Energy, E_0 (joules)	270	750	1270	1920	2430
Parameter A (μ -sec. $\text{cm}^{-3/2}$)	1.24	0.808	0.624	0.512	0.448
Arrival Time (μ -sec.)	155	101	78	64	56
Shock Velocity (mm/ μ -sec.)	1.07	1.65	2.14	2.61	2.98
(Mach No.)	2.38	3.68	4.75	5.79	6.62
Energy in Shock Wave, $\rho_0 R^2$ (joules/cm ²)	1.622	3.515	5.74	8.74	11.42
$\rho_0 R^2/E_0$ ($\times 10^{-3}$)	6.01	4.68	4.52	4.55	4.70

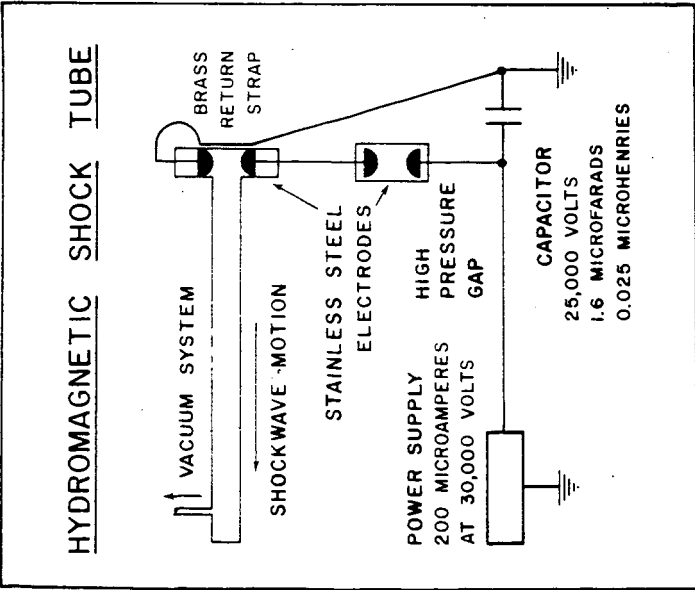


FIGURE 1.

SCHEMATIC ARRANGEMENT

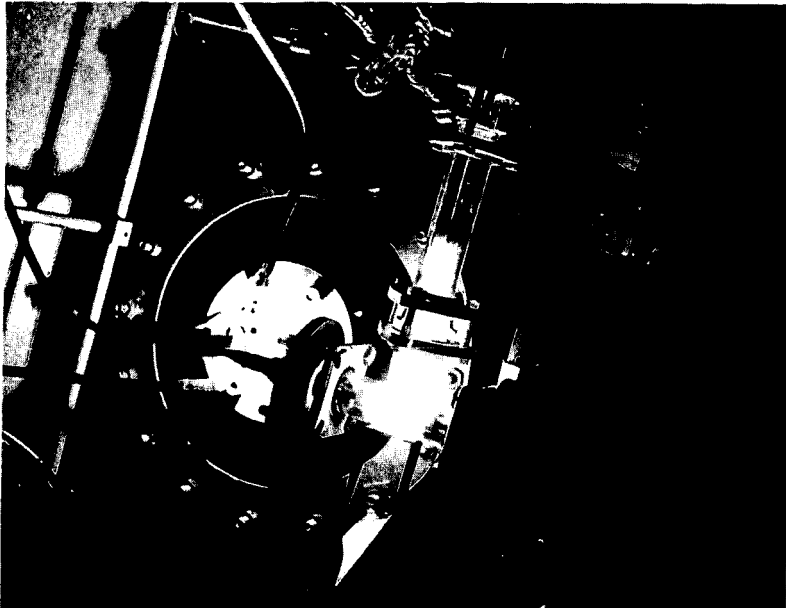


FIGURE 2.

A PHOTOGRAPH SHOWING PROPAGATION
OF THE LUMINOUS FRONT

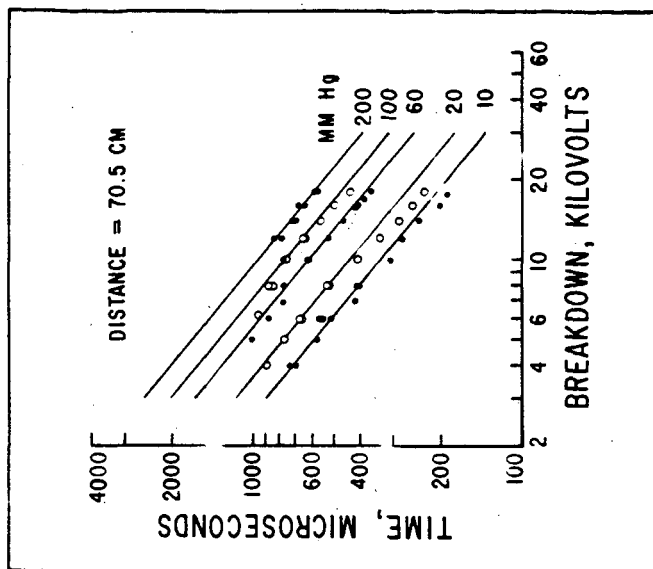


FIGURE 4.

SHOCK ARRIVAL TIMES IN NITROGEN

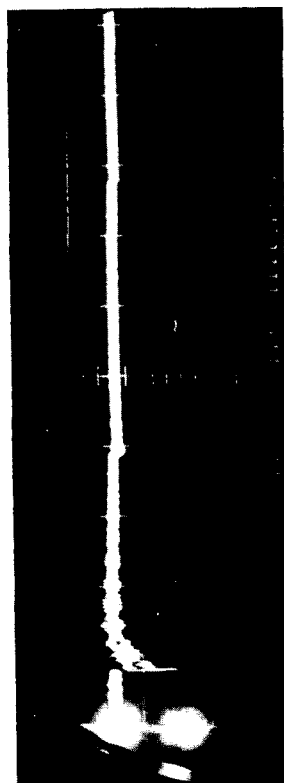


FIGURE 3.

OSCILLOGRAM SHOWING THE ARRIVAL
OF THE PRIMARY AND REFLECTED SHOCKS

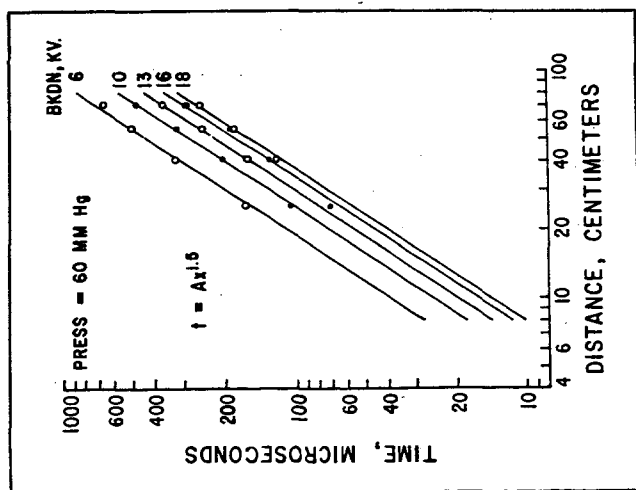


FIGURE 5.

SHOCK ARRIVAL TIMES IN METHANE

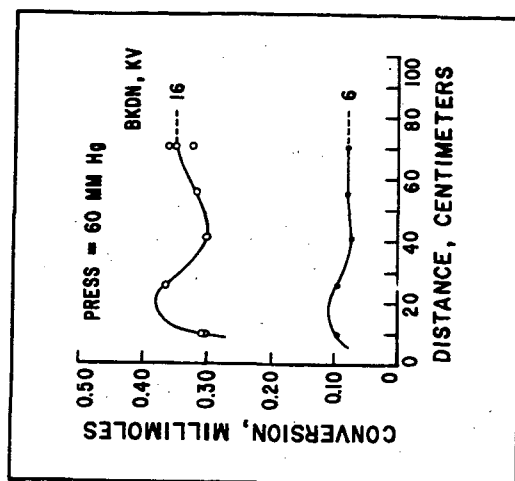


FIGURE 6.

EFFECT OF TUBE LENGTH
ON THE CONVERSION OF METHANE